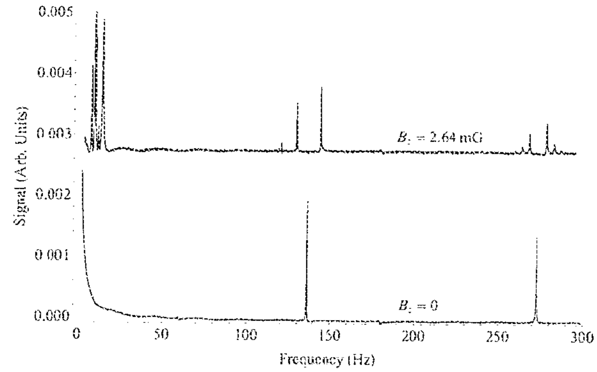


FIG. 3: Spectra for singly labeled acetonitrile-2, $^{13}CH_3CN$ in zero-field and in a field of 2.64 mG. The positions of all peaks are well described by Eqs. (3)-(7).

uncoupled proton due to an unknown solvent in the sample. The line at $J$ splits into a doublet, whose frequencies are given by Eq. (4), and the line at $2J$ splits into six lines, whose frequencies are given by Eq. (5). The splitting of the lines at $J$ and $2J$ clearly reveals the degeneracy of the zero-field levels. As with the formic acid spectrum, there is some asymmetry present in the multiplets centered about $J$ and $2J$, which is reproduced by numerical simulation. Nevertheless, the relative amplitudes of the lines centered about $2J$ are roughly in the ratio 1:3:6:6:3:1 as expected from first-order perturbation theory (see Supplementary Information).

To illustrate the utility of NZF NMR, we examine the case of fully labeled acetonitrile ($^{13}CH_3\,^{13}C^{15}N$). The zero field spectrum is shown in the bottom trace of Fig. 4. It is not immediately clear which lines correspond to which zero-field transitions. An expanded view of the zero-field spectrum in the range of 110 to 180 Hz is provided and compared to the spectrum obtained in the indicated finite magnetic fields. We see the appearance of doublets centered at 114, 126, and 151 Hz, indicating that these transitions occur between manifolds with $f = 0$ and $f = 1$. It is interesting to note that these doublets display different splittings due to differences in the Landé $g$ factors for the different manifolds involved in these transitions. The line at 131 Hz splits first into a doublet, which split into a pair of doublets. One can show that such a splitting pattern arises for a $f = 1 \leftrightarrow f = 1$ (see Supplementary Information). The small zero-field peak at 168 Hz splits into four lines, barely above the noise, indicating an additional $f = 1 \leftrightarrow f = 1$ transitions. Finally, the zero-field peak at 155.5 Hz splits into a sextet indicating the transition is $f = 1 \leftrightarrow f = 2$. The six lines in this multiplet appear "inside-out" compared to the six line multiplet observed at $2J$ in 2-acetonitrile due to a reversal in relative magnitude of the Landé $g$ factor.

The multiplicity of the peaks in this part of the spectrum can be understood as follows: Suppose we start